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ABSTRACT

Ferromanganese crusts, coatings of iron oxide and manganese (oxyhydr)oxide minerals, occur in various forms on a broad range of surface materials in the subaerial environment. Manganese (oxyhydr)oxide minerals in particular, have very high adsorption capacities for heavy metals and trace elements. Thus in the scenario whereby metals from ore deposits are liberated and mobilized to the surface and interact with ferromanganese crusts, there is potential for such crusts to adsorb anomalous concentrations of target and pathfinder elements, thereby offering a potential sampling medium during geochemical exploration.

Two case studies were undertaken at known base metal deposits, the >200 m deep Abra and <50 m deep Prairie-Wolf polymetallic deposits in the Capricorn Orogen terrane in Western Australia, where ferromanganese crusts are abundant at surface. Elemental mapping and microprobe analysis identified alternating laminae of Fe oxide and Mn (oxyhydr)oxide minerals in the crusts, and confirm the presence of Zn preferentially incorporated in Mn (oxyhydr)oxide layers. Selective leaching of Mn (oxyhydr)oxide within ferromanganese crusts followed by ICP-MS analysis yielded a broad range of results. High Zn/Mn ratios (>6 * 10⁻³) were returned from crusts proximal to the Prairie-Wolf deposits, and ratios in crusts decreased to as low as <1 * 10^{-3} with decreasing proximity to the mineralization. Ferromanganese crusts directly overlying mineralization at Abra, however, yielded low Zn/Mn ratios. This is interpreted to be a function of limited vertical mobilization of metals and preferential Mn scavenging in soils.

Our results suggest deposits which lie deep below the base of weathering that are geochemically-blind remain difficult to detect, but the analysis of ferromanganese crusts from semi-arid environments can be used to detect relatively shallow base metal mineralization.

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1. Introduction

1.1. Ferromanganese crusts

Abiotic and biogenic ferromanganese coatings and crusts composed of Fe oxides and Mn (oxyhydr)oxides (herein referred to as Fe-Mn crusts) exist almost ubiquitously in subaerial terrestrial environments within soils, sediments and as varnishes on rocks and caves, from equatorial to glaciated regions (Chao, 1972; Chao and Theobald, 1976; Post, 1999; Frierdich et al., 2011). These Fe-Mn crusts comprise a cosmopolitan range of Fe oxides and Mn (oxyhydr)oxide mineral phases (Chao and Theobald, 1976; Post, 1999), and may appear matte or lustrous black, brown or blue making them easily identifiable on surface materials.

* Corresponding author. *E-mail address:* sam.spinks@csiro.au (S.C. Spinks). Manganese oxide minerals are well known to have very high adsorption capacities for heavy metals and trace elements (Chao and Theobald, 1976; Means et al., 1978; Post, 1999; Brown et al., 1999; Brown and Parks, 2001; Manceau et al., 2007). Such adsorptive properties for target and pathfinder elements for mineral deposits led to Fe-Mn crusts, particularly in stream sediments in temperate climates, being tested as a potential exploration medium (Whitney, 1975; Chao and Theobald, 1976; Carpenter et al., 1975, 1978). During these studies Zn was determined to preferentially partition onto Mn (oxyhydr)oxide phases in Fe-Mn crusts in proximity to and downstream from known mineralization (Carpenter et al., 1975, 1978).

Ferromanganese crusts occur frequently in areas of the Capricorn Orogen of Western Australia, a frontier terrane with known base metal deposits but a relatively poor exploration history to date. Here we present two case studies from known base metal deposits in the Capricorn Orogen for the use of Fe-Mn crusts as a sink for anomalous Zn, and thus their feasibility as a geochemical exploration medium in a prospective semi-arid environment.

1.2. Geological setting and mineral exploration

The Capricorn Orogen of Western Australia was formed by the collision of the Archaean Yilgarn and Pilbara cratons from the Palaeoproterozoic to the Neoproterozoic, forming the Western Australian Craton (Johnson et al., 2013). The geology of the Capricorn Orogen (Fig. 1) comprises reworked Archaean metamorphic and igneous terranes, Proterozoic sedimentary basins (Fig. 2), and Mesoproterozoic mafic intrusives. Aside from the Glenburgh Terrane and Gascoyne Province in the west of the Capricorn Orogen, the surface geology of the majority of the central region is dominated by wellexposed sedimentary basin strata and intruded volcanics of the Edmund-Collier basin system of the Bangemall Supergroup (Figs. 1, 2). The degree and depth of surface weathering in the region are much less intense than in the Yilgarn Craton, which itself has been subject to extreme chemical weathering over millions of years down to several hundred metres in depth (Anand and Paine, 2002; Anand and Butt, 2010). The scarcity of intense weathering in the Capricorn Orogen has arguably affected the exploration success in the region due to the lack of widespread weathering intersecting mineral deposits, which restricts widespread dispersion of target and pathfinder elements close to surface (Anand and Butt, 2010). Rather, the sedimentary basin rocks of the region are often well cemented or locally-altered and can act as a robust geochemical seal, inhibiting large-scale dispersion of potential sediment-hosted mineralization pathfinder elements to the surface (Anand and Paine, 2002; Anand and Butt, 2010). This can inhibit geochemical exploration at the surface. Thus, conduits for potential leakage of pathfinder elements such as fault zones, may be one of few



Fig. 1. Simplified geological map of the major units of the Capricorn Orogen of Western Australia. Dashed lines delineate approximate contact between Archaean Pilbara and Yilgarn crators to the north and south, respectively. Case study sites at Prairie-Wolf and Abra base metal deposits are highlighted by box insets, and their local detailed geology is shown in Figs. 6 and 7. Map data extracted from the Geological Survey of Western Australia *1:2.5 M Tectonic Unit 2015* dataset, (GSWA, 2015). © 2016 CSIRO. All Rights Reserved.

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