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Chemical and isotopic signatures of waters associated with the carbonation of ultramafic mine tailings, Woodsreef Asbestos Mine, Australia

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ABSTRACT

Extensive carbonate crusts have formed on the tailings of the Woodsreef Asbestos Mine, sequestering significant amounts of CO_2 directly from the atmosphere. The physico-chemical (pH, T, conductivity), chemical (cations, dissolved inorganic carbon (DIC)) and isotopic (δ^2H, $\delta^{18}O$, $\delta^{13}C_{DIC}$, $F^{14}C$) signatures of waters interacting with the tailings and associated carbonate precipitates provide insight into the processes controlling carbonation. We observe two distinct evolutionary pathways for a set of stream and meteoric-derived water samples, respectively, with both groups generally being characterised as moderately alkaline, bicarbonate-dominated and Mg-rich waters. Stream water samples are supersaturated with CO_2 and therefore prone to degassing, which, in combination with evaporation, drives carbonate supersaturation and precipitation. Isotopic signatures indicate soil CO_2 as the main carbon source in the stream waters entering the tailings pile, whereas water emerging downstream of the tailings pile may also contain carbon from the dissolution of isotopically light bedrock magnesite in an open system with respect to soil CO_2. The evolution of meteoric-derived waters on the other hand, partly occurs under CO_2-limited conditions, which results from reduced CO_2 ingress at depth and/or a temporal lag between fluid alkalisation and kinetically hindered uptake of CO_2 into alkaline solution. A high pH, Mg-rich meteoric water absorbs atmospheric CO_2 after discharging into a tunnel within the tailings pile, resulting in high DIC concentrations with atmospheric carbon isotope signature. Evaporation of the water at the discharge point in the tunnel drives precipitation of hydromagnesite ($Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$), displaying a clear atmospheric isotope signature, broadly consistent with previous estimates of carbon and oxygen isotope fractionation during precipitation of hydrated Mg-carbonate.

1. Introduction

An earlier study has shown that, weathering of the mine tailings at the Woodsreef Asbestos Mine, NSW, Australia results in the formation of extensive carbonate crusts and cements (Oskierski et al., 2013a). The crusts, consisting mainly of hydromagnesite, predominantly incorporate CO_2 of atmospheric origin, as evidenced by high $\delta^{13}C$ and $F^{14}C$. Weathering-related carbonation of silicate rocks is considered an important process for the stabilisation of Earth's climate and contributes significantly to the removal of CO_2 from the atmosphere (Gaillardet et al., 1999; Ruddiman, 2013). Quantification of carbonate content in ultramafic tailings based on quantitative X-ray diffraction demonstrates that carbonation proceeds at significantly higher rates than background CO_2 uptake rates by chemical weathering of coherent silicate rock (Oskierski et al., 2013a; Wilson et al., 2009; Wilson et al., 2011; Wilson et al., 2014). Consequently carbonation of ultramafic mine tailings provides a viable option for low-energy, low-cost sequestration of atmospheric CO_2, which has the potential to make a relevant contribution to international efforts in reducing CO_2 concentrations in the atmosphere (Assima et al., 2014a; Assima et al., 2014b; Power et al., 2013; Power et al., 2014; Pronost et al., 2011; Wilson et al., 2006; Wilson et al., 2014).

Since dissolution of tailings minerals and precipitation of carbonate occur in the aqueous phase, water samples provide valuable insight into the processes controlling carbonation. Water samples represent an intermediate step in the aqueous carbonation process and thus add detail to the understanding of natural carbonation of mine tailings during weathering, which has so far been largely based on mineralogy and isotopic signatures of solid samples (Oskierski et al., 2013a; Pronost et al., 2012; Wilson et al., 2006; Wilson et al., 2009), except for a study of biogeochemical processes in hydromagnesite playas (Power et al., 2009) and of water infiltrating peridotite-hosted mine shafts (Beinlich and Austrheim, 2012). Reactive transport models have been used to

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derive a better understanding of the formation of alkaline, Ca–OH waters emanating from ultramafic rocks (Bruni et al., 2002; Cipolli et al., 2004; Marques et al., 2008; Paukert et al., 2012) and more recently these models are also applied to the carbonation of ultramafic mine tailings (Bea et al., 2011; Harrison et al., 2015; Wilson et al., 2014).

In this contribution, we integrate sampling context, field parameters, water chemistry and isotopic information on carbon sources and evaporation to derive insight into the evolution of water samples associated with the carbonation of mine tailings at Woodsreef, with special emphasis on carbonate precipitation. Enhanced understanding of carbonation of mine tailings aims to identify rate-limiting steps in the carbonation process in order to engineer tailings storage facilities optimised for the purpose of CO_2 sequestration (Assima et al., 2012; Assima et al., 2013a; Assima et al., 2014a; Assima et al., 2014b; Gras et al., 2015; Gras et al., 2015; Lechat et al., 2015; Lechat et al., 2016; McCutcheon et al., 2015; Power et al., 2013; Power et al., 2014; Pronost et al., 2011; Pronost et al., 2012; Wilson et al., 2014).

2. Study site

2.1. Geology

The Woodsreef Asbestos Deposit, New South Wales, Australia, is located in the southern part of the New England Orogen, which stretches along the central area of the east coast of the Australian continent (Fig. 1). The deposit is a chrysotile mineralisation hosted in the ultramafic rocks of the Great Serpentinite Belt, a disrupted ophiolite sequence which has been tectonically emplaced along the Peel–Manning Fault system. The Woodsreef serpentinite predominantly consists of schistose and massive serpentinite, as well as partially serpentinised harzburgite (Glen and Butt, 1981). Chrysotile was extracted from the deposit intermittently between 1906 and 1983, producing 24.2 Mt of ultramafic tailings (Brown et al., 1992). The tailings result from dry-grinding of chrysotile ore and are stored above ground on an area covering about 0.5 km^2 (Svanosio, 2000; Fig. 1).

On the western side the Woodsreef serpentinite, a thin layer of magnesite and chlorite creates a sharp boundary to the sandstones of the Tamworth Belt, while the eastern boundary to the rocks of the Woolomin group is much more irregular (Glen and Butt, 1981). Siliceous argillites, chert and jasper, with minor diamictites and metabasalt of the pelagic Nangarah and Bobs Creek Formations constitute the lithologies of the Woolomin Group to the east of the Woodsreef serpentinite (Vickery et al., 2010). For a detailed description of the geology of the study area and the chrysotile mineralisation the reader is referred to Glen and Butt (1981); O'Hanley and Offler (1992) and Vickery et al. (2010).

2.2. Mineralogy

The mineralogy of the tailings pile at Woodsreef is a result of several stages of alteration, including serpentinisation–recrystallisation, hydrothermal alteration and weathering of the bedrock (Ashley and Brownlow, 1993; Ashley, 1997; Kmetoni, 1984; O'Hanley and Offler,

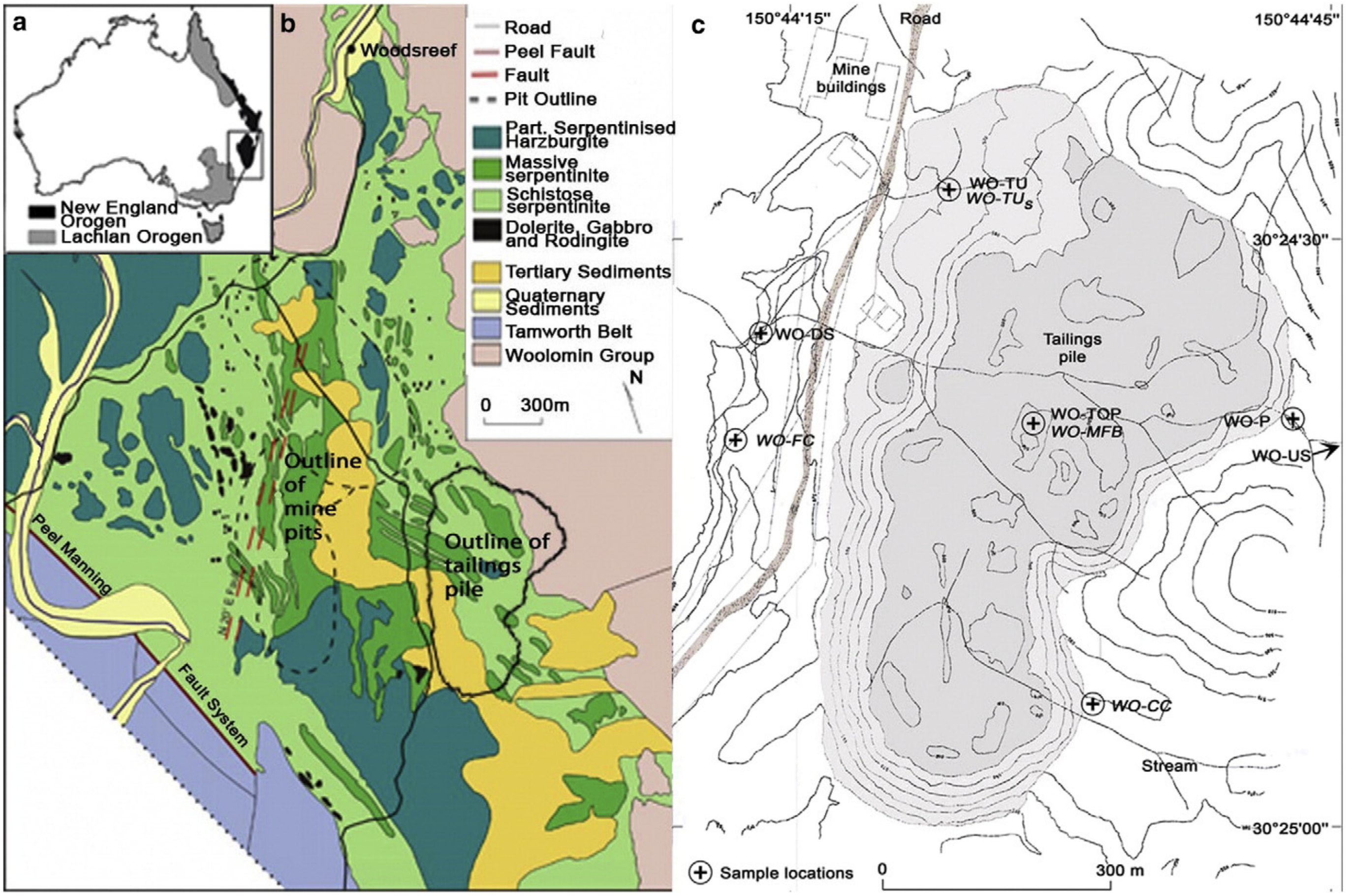

Fig. 1. Geology and sample locations (modified from Oskierski et al., 2013a). a. Location of the Southern New England Orogen (modified from Guo et al., 2007). b. Detailed geology of the Woodsreef serpentinite (modified from Davis, 2008 and Glen, 1971). c. Topography of tailings pile and sampling locations (modified from Svanosio, 2000).