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Paleoenvironmental and paleohydrochemical conditions of dolomite formation within a saline wetland in arid northwest Australia

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A B S T R A C T

Groundwater dolocrete occurring within the Fortescue Marsh, a large inland wetland in the Pilbara region of northwest Australia, has been investigated to provide paleoenvironmental and paleohydrological records and further the understanding of low temperature dolomite formation in terrestrial settings over the Quaternary Period. Two major phases of groundwater dolocrete formation are apparent from the presence of two distinct units of dolocrete, based on differences in depth, $\delta^{18}O$ values and mineral composition. Group 1 (G1) occurs at depth 20–65 m b.g.l. (below ground level) and contains stoichiometric dolomite with $\delta^{18}O$ values of −4.02–0.71‰. Group 2 (G2) is shallower (0–23 m b.g.l.), occurring close to the current groundwater level, and contains Ca-rich dolomite ± secondary calcite with a comparatively lower range of $\delta^{18}O$ values (−7.74 and −6.03‰). Modelled $\delta^{18}O$ values of paleogroundwater from which older G1 dolomite precipitated indicated highly saline source water, which had similar stable oxygen isotope compositions to relatively old brine groundwater within the Marsh, developed under a different hydroclimatic regime. The higher $\delta^{18}O$ values suggest highly evaporitic conditions occurred at the Marsh, which may have been a playa lake to saline mud flat environment. In contrast, G2 dolomite precipitated from comparatively fresher water, and modelled $\delta^{18}O$ values suggested formation from mixing between inflowing fresher groundwater with saline-brine groundwater within the Marsh. The $\delta^{18}O$ values of the calcite indicates formation from brackish to saline groundwater, which suggests this process may be associated with coeval gypsum dissolution. In contrast to the modern hydrology of the Marsh, which is surface water dependent and driven by a flood and drought regime, past conditions conducive to dolomite precipitation suggest a groundwater dependent system, where shallow groundwaters were influenced by intensive evaporation.

1. Introduction

Dolomite, $CaMg(CO_3)_2$, is a relatively common mineral in carbonate deposits worldwide, mostly within marine dolostone formed by replacement of limestone. However, in recent decades dolomite has been recognised more frequently in continental sediments, often occurring in saline evaporitic environments in proximity to saline lakes or playas, in arid climates (Müller et al., 1972; Last, 1990). Surficial dolomite precipitates from carbonate-rich ground or surface waters and encompasses a variety of forms including palustrine and lacustrine dolomite precipitated in wetlands and lakes (Alonso-Zarza, 2003) as well as groundwater and pedogenic dolomite that develop by replacement and cementation processes in the phreatic to vadose zone (Wright and Tucker, 1991). However, the processes controlling dolomite precipitation and dolomitization in terrestrial environments remain largely unknown. Precipitation of dolomite is strongly controlled by reaction kinetics and is inhibited at surface temperatures and pressures (Morrow, 1982a), although laboratory studies by Vasconcelos et al. (2005) and Wright and Wacey (2005) have demonstrated primary dolomite precipitation in the presence of sulfate-reducing bacteria. More recently, Zhang et al. (2012a; 2012b) observed abiotic nucleation and growth of disordered dolomite from high dissolved sulfide solution and later with dissolved polysaccharides; and Roberts et al. (2013) demonstrated carboxyl groups may promote the nucleation of dolomite as Mg-ions are dewatered and bound to

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the carboxyl sites, overcoming the kinetic barriers of precipitation. These observations raise the question as to what hydrological conditions and environments may promote dolomite formation.

The presence of dolomite indicates specific hydrochemical conditions that have favoured dolomite formation, including elevated Mg/Ca, high salinity and high alkalinity and therefore, high CO_3^{2-} activity (Folk and Land, 1975; Morrow, 1982a; Hardie, 1987; De Deckker and Last, 1988). Evaporative concentration combined with calcite precipitation along a hydrological flow path results in increasingly saline groundwater and higher Mg/Ca waters, which may ultimately precipitate dolomite (Arakel, 1986; Jones and Deocampo, 2003). Degassing of CO_2 from emerging waters at groundwater discharge zones also promotes carbonate precipitation as it decreases total carbonate species, while carbonate alkalinity remains constant, resulting in increasing pH of groundwater during evaporative concentration and subsequently higher CO_3^{2-} activity (Eugster, 1980; Morrow, 1982a). Dolomite may therefore, occur in depressions towards the centre of drainage basins and at groundwater discharge zones (Mann and Horwitz, 1979). Higher Mg/Ca ratios in groundwater may also occur in basins where there has been weathering of high-Mg rocks, such as marine dolomite or Mg-rich volcanics (Last and De Deckker, 1990; Alonso-Zarza and Martín-Pérez, 2008; Jones et al., 2009; Dogramaci and Skrzypek, 2015). Groundwater calcrete and dolocrete (based on the genetic classification of calcrete types by Carlisle (1983), but pertaining to deposits composed dominantly of dolomite), have been previously identified as part of the continuum of groundwater precipitates along drainage and paleodrainage systems of inland Australia and are often tens of metres thick and laterally expansive (Mann and Horwitz, 1979; Arakel and McConchie, 1982; Arakel, 1986). Groundwater dolocretes have also been recognised within alluvial sediments in the Paris Basin (Thiry, 1989; Spötl and Wright, 1992) and Provence Basin (Colson and Cojan, 1996) in inland France; in the Sado and Lisbon Basin in Portugal (Pimentel et al., 1996); and in the coastal region of Kuwait along the Arabian Gulf (Khalaf, 1990; El-Sayed et al., 1991). The models presented for groundwater dolocrete formation highlight the importance of groundwater hydrochemical evolution in the lower reaches of closed basins (Mann and Horwitz, 1979; Arakel, 1986; Armenteros et al., 1995) as well as mixing between relatively fresh groundwater with saline groundwater, commonly surrounding saline-playa lakes in evaporitic basins (Colson and Cojan 1996; Jutras et al., 2007) but also marine groundwaters in coastal environments (El-Sayed et al., 1991; Williams and Krause, 1998; Khalaf et al., 2017). The mixing of groundwaters increases the alkalinity, which both increases silica solubility and reduces dolomite solubility, favouring replacement of silicate host sediments by dolomite (Arakel and McConchie, 1982; Deelman, 2003). The previous studies of groundwater dolocrete have suggested that local groundwater chemistry was most likely conducive to direct or early diagenetic dolomite formation resulting in dolocretization of host sediments, evidenced by primary dolomite euhedral crystals and lack of calcite precursors (Arakel, 1986; Khalaf, 1990; El-Sayed et al., 1991; Spötl and Wright, 1992). This is in contrast to dolomitic horizons occurring within groundwater calcrete profiles, formed by dolomitization of calcite, usually within the capillary zone where evaporation has the greatest effect on shallow groundwater (Arakel, 1986). Dolocretes remain largely undocumented in comparison to calcretes and have also been neglected in the investigation of terrestrial dolomite formation, which has mostly focussed on lacustrine dolomite occurring in proximity of the coastline and influenced by marine groundwaters (Clayton and Jones, 1968; Rosen et al., 1989; Rosen and Coshell, 1992). Groundwater dolocrete within inland continental settings may therefore provide new insights into the mechanisms of dolomite formation in terrestrial environments.

The chemistry and stable isotopic composition of carbonate minerals are indicative of the hydrochemical conditions in which they precipitated (Craig, 1953; Emrich et al., 1970; Vasconcelos et al., 2005) and have been used successfully as a tool for paleoenvironmental reconstruction (eg. Hays and Grossman, 1991; Hays and Kyser, 2001; Deutz et al., 2001; Bustillo et al., 2002; Alonso-Zarza, 2003; Cyr et al., 2005; Bowen et al., 2008). Groundwater dolocrete associated with evaporitic basins in inland settings provides an important continental archive of paleoenvironmental and paleohydrological conditions, which has thus far been largely overlooked. A unique drilling program, conducted in 2011 by Rio Tinto Iron Ore at the Fortescue Marsh, a large inland wetland in the Pilbara region of northwest Australia, revealed dolocrete deposits of up to 20 m thick occurring with the Marsh sediments. This provided a new opportunity to utilise dolomite geochemistry to improve our understanding of the physiochemical environments and hydrological processes involved in groundwater dolocrete formation and therefore, advance knowledge of the conditions of terrestrial dolomite formation and provide paleoenvironmental and paleohydrological records. In this study we investigate the geochemistry and stable isotope compositions of dolomite and groundwater from various depths within the Marsh to; 1) produce a first assessment of the mineralogy and geochemistry of dolocrete within the Marsh; 2) understand the hydrological processes and chemical conditions resulting in dolocrete formation; and 3) utilise this information to produce records of paleoenvironmental and paleohydrological conditions.

2. Site description

2.1. Geological setting

The Fortescue Marsh is an ephemeral wetland located in the semi-arid Hamersley Basin in the Pilbara region of northwest Western Australia (Fig. 1). The basement under the Marsh is composed of crystalline blue-grey dolomite of the Wittenoom Formation (Barnett and Commander, 1985; Skrzypek et al., 2013).

The incision of the Hamersley Basin sedimentary rocks in the Late Cretaceous to Paleogene, under a more humid climate, resulted in the formation of the Fortescue Valley paleodrainage (Barnett, 1981; Macphail and Stone, 2004). The Marsh occupies the lowest part (~400 m a.s.l), extending over ~1100 km^2 between the Chichester and Hamersley Ranges in the Eastern Fortescue Valley and is the terminal basin of the Upper Fortescue River (Skrzypek et al., 2016). The Marsh is separated from the Lower Fortescue River by the Goodiadarrie Hills, located on the western edge of the Marsh (Fig. 1). The Fortescue Valley lowlands have filled with Cretaceous to Holocene alluvium and colluvium (Barnett, 1981). Barnett (1981) described the sediments of the Western Fortescue Valley in the adjacent Lower Fortescue River catchment and found a sequence of colluvial, alluvial and lacustrine sediments of up to 120 m thick. The sediments grade from Cretaceous to Paleogene iron-rich pisolitic and conglomerate fluvial and channel fill sediments overlying the Wittenoom Formation basement, through dolomite of the Millstream Formation, lacustrine clay and alluvial sediments (Barnett, 1981). Unconsolidated Quaternary alluvial and colluvial clay and silt sediments of up to ~30 m cover much of the valley (Barnett, 1981). However, due to the remote nature of the Marsh in the Eastern Fortescue Valley, lack of mineral resources in the Marsh itself and protection due to environmental and heritage significance, there is very limited information on the specific nature of the Fortescue Marsh sediments. The drilling program conducted by Rio Tinto Iron Ore in 2011, provided the first overview of the distribution of sediments within the Marsh, revealing ~15–80 m of alluvium, colluvium and chemical sediments overlying the Wittenoom